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Double relaxation of straight chain alcohols under high frequency electric field

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Abstract : Alcohols like 1-butanol, 1 hexanol, 1-heptanol and 1-decanol are long straight chain polar molecules almost like polymers. In these alcohols as well as in methanol and ethanol, there exist many possibilities of having internal rotation, bending and twisting, each with a characteristic relaxation time, under high frequency electric field of Giga hertz range. An attempt is, therefore, made to detect the double relaxation phenomena by the new approach suggested earlier. It involves single frequency measurements of the dielectric relaxation data of those compounds in solvent n-heptane at 25°C under three different frequencies of 24.33, 9.25 and 3.00 GHz electric field as well as those of methanol and ethanol in benzene at 9.84 GHz respectively to get τ_1 and τ_2 for their flexible parts and the whole molecules. The alcohols under investigation, always exhibit the double relaxation behaviours at all frequencies except methanol at 9.84 GHz, thus indicating separate broad dispersions in them. The relative contributions c_1 and c_2 towards dielectric relaxations due to τ_1 and τ_2, are calculated from Frohlich's equations to compare with those as obtained by graphical technique. The dipole moments μ's are also estimated in terms of the relaxation times τ_1 and τ_2, obtained from the slopes β's of the hf conductivities K_{ij}'s of the solutions against the weight fraction w_j's of the solutes in order to support their usual conformations.

Keywords : Double relaxation, dipole moments, straight chain alcohols

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1. Introduction

The dielectric relaxation phenomena of highly nonspherical polar liquids in nonpolar solvents under the ultra high frequency (uhf) electric fields have gained much attention [1,2] as they reveal various types of molecular interactions like solute-solute (dimer) and solute-solvent (monomer) formations in liquid mixtures. They also provide one with

The nomenclature of symbols used, are given in the Appendix.

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valuable information regarding sizes, shapes, structures and different thermodynamic parameters due to relaxation of the polar liquids [3].

The relaxation phenomena of pure primary alcohols are very interesting as they were found to possess three distinct low frequency Debye type processes predicting inherently the single relaxation time [4,5]. The dilution of polar alcohols with nonpolar solvents, however, increases the relative contributions towards dielectric dispersions in the hf electric field [6]. The straight chain mono-alcohols, on the other hand, are almost like polymers having $-CH_3$ and $-OH$ groups in their structures. Obviously, there exist many possibilities of internal and molecular rotations, bending, twisting *etc* each with a characteristic relaxation time. In averaging to the macroscopic condition, a distribution of relaxation time may also be possible. Mishra *et al* [7] claimed that it is not possible to resolve dielectric dispersion in three relaxation processes from the measured relaxation data under a single frequency electric field

Again, to detect the double relaxation phenomena of a polar solute, Bergmann *et al* [8] proposed a technique based on measured relaxation parameters of pure polar liquid like real ε', loss ε'' of the complex dielectric constant ε^* as well as static ε_0 and the high frequency dielectric constant ε_∞ at different frequencies of the electric field. The term $\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty}$ was then plotted against $\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty}$ following Cole-Cole semi-circle equation. A suitable chord joining the two fixed points on the semi-circle consistent with all the experimental points is then chosen to yield the relaxation time τ_1 and τ_2 of the flexible part and the whole molecule itself. Bhattacharyya *et al* [9] had subsequently modified the procedure of Bergmann *et al* [8] to get τ_1 and τ_2 of a pure polar liquid in terms of the relaxation parameters measured at two different frequencies of the electric field in the GHz range.

In such a context, we have studied the double relaxation phenomena of some straight chain aliphatic alcohols, namely 1-butanol, 1-hexanol, 1-heptanol and 1-decanol dissolved in n-heptane at 24.33, 9.25 and 3.00 GHz electric field together with methanol and ethanol dissolved in benzene at 9.84 GHz electric field respectively at a temperature of 25°C by the recently developed method [10]. It is usually made with the single frequency measurements of the dielectric relaxation parameters like ε'_{ij}, ε''_{ij}, ε_{0ij} and $\varepsilon_{\infty ij}$ of a polar solute (j) in a nonpolar solvent (i) for different weight fractions w_j's of the polar solute. τ_1 and τ_2 are then obtained from the slope and the intercept of a straight line equation containing the dielectric relaxation data of which ε_{0ij} and $\varepsilon_{\infty ij}$ should be accurately known [11]. The approach as suggested earlier [10], seems to be an effective tool to detect the double relaxation phenomena of the polar liquid in a nonpolar solvent within the framework of Debye and Smyth model. For such straight chain alcohols behaving almost like polymers, Onsager's equation may be a better choice due to the strong intermolecular force exerted by alcohols in solution owing to their high dipole moments. But the resulting expressions can not be solved so easily as has been done in [10], because of the presence of the quadratic term ε^*_{ij}. The method [10] was already applied to mono-substituted anilines [12] in benzene in order

Table 1. The estimated intercept and slopes of straight line equation $\left[(\varepsilon_{0ij} - \varepsilon'_{ij})/(\varepsilon'_{ij} - \varepsilon_{\infty ij})\right]$ against $\left[\varepsilon''_{ij}/(\varepsilon'_{ij} - \varepsilon_{\infty ij})\right]$ with errors and correlation coefficients together with measured τ's of some normal alcohols at 25°C under different ultra high frequency (~ gigahertz) electric field

System with Sl. No and molecular wt.	Frequency f in GHz	Intercept and slope of equation (8)		Correlation coefficient (r)	Percentage error in regression technique	Estimated values of τ_2 and τ_1 in p Sec		Measured τ_1 in p Sec	Most probable relaxation time $\tau_0 = \sqrt{\tau_1 \tau_2}$ in p Sec
I) 1-Butanol in	(a) 24 33	2 6046	8 6557	0 9013	5 16	54 60	2.04	1 96	10.55
n-heptane	(b) 9 25	1.2809	6 1343	0 9347	3 47	101 87	3 73	4 30	19 49
$M_j = 74$ gm	(c) 3 00	0.6825	4.1544	0.9328	3 57	211 41	9.10	16.98	43.86
II) 1-Hexanol in	(a) 24.33	2 045	6 7079	0.6195	18 58	41 81	2 10	2.74	9.37
n-heptane	(b) 9 25	1 0803	5.1697	0 9163	4 42	85 24	3.76	5 86	17.90
$M_j = 102$ gm	(c) 3 00	0 6651	4 0210	0.9308	3 67	204 26	9 17	13.14	43 28
III) 1-Heptanol in	(a) 24 33	2.8273	7.9933	0.6752	14.98	49.89	2.43	2.11	11 01
n-heptane	(b) 9.25	0.9233	5.0147	0 9433	3 03	83 03	3.30	5 78	16.55
$M_j = 116$ gm	(c) 3 00	0.6823	4.1075	0 9638	1 95	208 81	9.20	13 49	43.83
IV) 1-Decanol in	(a) 24 33	2.4813	5 4316	0 8153	9.23	32.25	3.30	2.69	10.32
n-heptane	(b) 9.25	1 5735	5 1553	0.9463	2 87	83 14	5.61	5.71	21.60
$M_j = 158$ gm	(c) 3.00	0.3316	2.6855	0.9228	4.08	135 66	6.89	14.37	30.57
V) Ethanol in benzene									
$M_j = 46$ gm	9 84	4.5211	288.7386	0 9416	3 42	4672.26	0 25	3.9	34 18
VI) Methanol in benzene									
$M_j = 32$ gm	9 84	–5.4003	198 2809	0 8952	5 99	3209.12	—	4.3	—

Table 2. Fröhlich parameter A, relative contributions c_1 and c_2 due to τ_1 and τ_2, theoretical values of x and y due to Frohlich eqs (9) and (10) and those by our method at infinite dilution for monoalcohols under different uhf electric field at 25°C

System with Sl No and molecular wt		Frequency f in GHz	Frohlich parameter $A = \ln(\tau_2/\tau_1)$	Theoretical values of x and y from eq no (9) and (10)		Theoretical values of c_1 and c_2 from eq no (4) and (5)		Estimated values of x and y at $w_j \to 0$ from Figs. (2) and (3)		Estimated values of c_1 and c_2 from graphical technique	
I) 1-Butanol in	(a)	24 33	3 2871	0 3666	0 3495	0 3701	2 0678	0.83	0 218	0 9162	–0 3579
n-heptane	(b)	9 25	3 3073	0 4651	0 3596	0 4394	1 6354	0 99	0 15	1.0483	–0.4076
M_J = 74 gm	(c)	3 00	3 1455	0 5556	0 3670	0 4985	1 2024	1 11	0 13	1 1589	–0 2668
II) 1-Hexanol in	(a)	24 33	2 9912	0 3924	0 3692	0 3885	1 6769	0 79	0 264	0 8694	0 0725
n-heptane	(b)	9 25	3 1211	0 4885	0 3704	0 4535	1 4215	0 70	0 130	0 7385	–0 1234
M_J = 102 gm	(c)	3 00	3 1035	0 5600	0 3689	0 5004	1 1707	1 005	0 078	1 0618	–0 4113
III) 1-Heptanol in	(a)	24.33	3 0219	0 3464	0 3588	0 3580	1 8763	0 655	0 236	0 7464	–0 0586
n-heptane	(b)	9.25	3 2253	0 5112	0.3647	0 4703	1 3973	0 835	0 130	0 8724	–0.1575
M_J = 116 gm	(c)	3.00	3 1222	0 5560	0 3682	0 4983	1 1910	1 045	0 116	1.0942	–0 2853
IV) 1-Decanol in	(a)	24 33	2 2796	0.3412	0 3962	0.3644	1.2809	1 11	0 29	1 4687	–1.5413
n-heptane	(b)	9 25	2 6960	0 4268	0 3899	0 4105	1 3544	0.955	0 17	1.0911	–0 7627
M_J = 158 gm	(c)	3.00	2 9801	0 6640	0.3585	0 5611	0 8453	1.005	0 012	1.0716	–0 3678
V) Ethanol in benzene											
M_J = 46 gm		9.84	9 8357	0 4240	0 1577	0 4236	43.6436	0.24	0.0099	0 2400	1.7937

to get the frequency dependence of τ_1 and τ_2 under three different electric fields of 22.06, 3.86 and 2.02 GHz respectively, showing either the double or the mono-relaxation behaviours. *p*-anisidine alone shows the mono-relaxation behaviour at all frequencies. When the data are extended to 9.945 GHz electric field, all of them, on the other hand, show the double relaxation phenomena [13]. No such rigorous study on monohydric alcohols has been made so far. So it seems worthwhile to make an extensive study on the available data of aliphatic alcohols [14] as well as ethanol and methanol [15,16] with special emphasis on possible occurrence of τ_1 and τ_2 in the hf electric field [6].

It is evident from Table 1 and Figure 1 that all the alcohols show the double relaxation phenomena in all the frequencies of GHz range except methanol at 9.84 GHz, indicating separate broad dispersions in them. Ethanol is a system with $\tau_2 \rangle\rangle \tau_1$ while methanol shows very high value of τ_2 only. τ_1 and τ_2 are compared with most probable relaxation time τ_0 where $\tau_0 = \sqrt{\tau_1 \tau_2}$ as shown in the last column of Table 1. In absence of accurate τ for such alcohols, τ's are estimated from the slope of the imaginary part K''_{ij} and the real part K'_{ij} of the total uhf conductivity K^*_{ij} and placed in the 9th column of Table 1 for comparison with τ_1, τ_2 and τ_0 respectively.

The relative contributions towards the dielectric relaxation *i.e.* c_1 and c_2 due to τ_1 and τ_2 are estimated by using Fröhlich's equations [17] as well as graphical method (Figures 2 and 3). They are also shown in Table 2.

The dipole moments μ_1 and μ_2 of the flexible part as well as of the whole molecule are then estimated in terms of τ and slope β of the linear plot of K_{ij} against w_j (Figure 4). They are shown in Table 3 in order to compare with μ_0 due to τ_0 and μ_{theo} from bond angles and bond moments (Figure 5) respectively. The μ_1's in terms of c_1, c_2 and μ_2 are also calculated by assuming that the two relaxation processes are equally probable; and they are placed in the last column of Table 3 only to compare with μ_1 due to τ_1.

2. Theoretical formulations to estimate $\tau_1, \tau_2; c_1, c_2$ and μ_1, μ_2

The complex dielectric constant ε^*_{ij} of a polar non-polar liquid mixture can be represented as the sum of a number of non-interacting Debye type dispersions in accordance with the Budo's [18] relation as :

$$\frac{\varepsilon^*_{ij} - \varepsilon_{\infty ij}}{\varepsilon_{0ij} - \varepsilon_{\infty ij}} = \sum_k \frac{c_k}{1 + j\omega\tau_k}, \tag{1}$$

where $j = \sqrt{-1}$ and $\Sigma c_k = 1$. The term c_k is the weight factor for the k-th type of relaxation mechanism. When the complex dielectric constant ε^*_{ij} consists of two non-interacting Debye type dispersions, Budo's relation reduces to Bergmann's [8] equations :

$$\frac{\varepsilon'_{ij} - \varepsilon_{\infty ij}}{\varepsilon_{0ij} - \varepsilon_{\infty ij}} = \frac{c_1}{1 + \omega^2\tau_1^2} + \frac{c_2}{1 + \omega^2\tau_2^2} \tag{2}$$

and
$$\frac{\varepsilon''_{ij}}{\varepsilon_{0ij} - \varepsilon_{\infty ij}} = c_1 \frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + c_2 \frac{\omega\tau_2}{1 + \omega^2\tau_2^2}, \tag{3}$$

such that $c_1 + c_2 = 1$, where c_1 and c_2 are the relative contributions towards dielectric relaxations due to intra-molecular relaxation time τ_1 and molecular relaxation time τ_2.

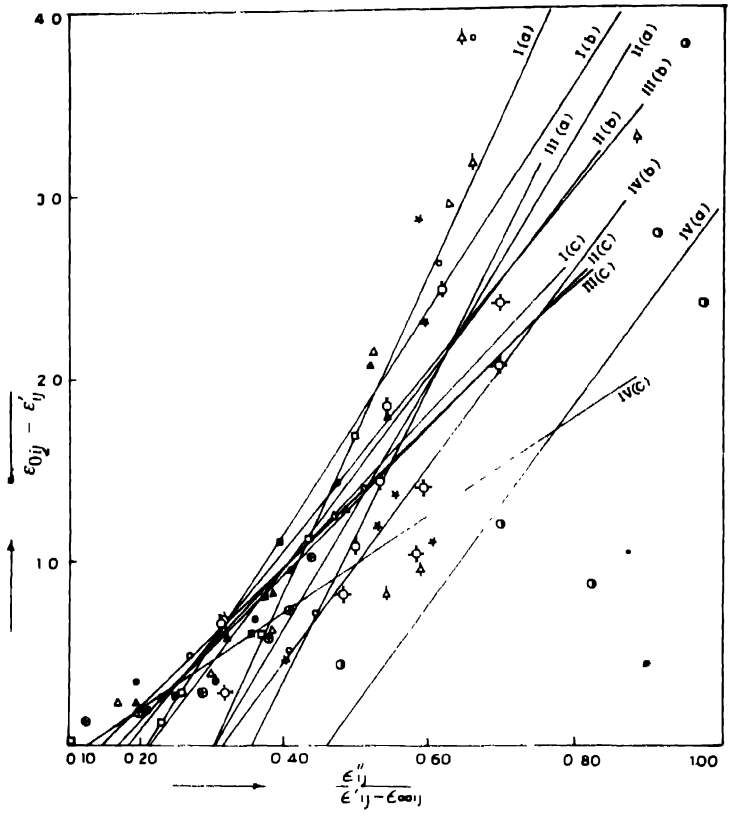

Figure 1. Straight line plots of $(\varepsilon_{0ij} - \varepsilon'_{ij})/(\varepsilon'_{ij} - \varepsilon_{\infty ij})$ against $\varepsilon''_{ij}/(\varepsilon'_{ij} - \varepsilon_{\infty ij})$ of monoalcohols at 25°C under different *uhf* electric field.

System I (a) —O—O— for 1-Butanol at 24 33 GHz.
I (b) —Δ—Δ— for 1-Butanol at 9 25 GHz.
I (c) —□—□— for 1-Butanol at 3 00 GHz
System II (a) —Δ—Δ— for 1-Hexanol at 24 33 GHz
II (b) —○—○— for 1-Hexanol at 9.25 GHz
II (c) —●—●— for 1-Hexanol at 3.00 GHz.
System III (a) —✱—✱— for 1-Heptanol at 24 33 GHz
III (b) —▲—▲— for 1-Heptanol at 9.25 GHz
III (c) —■—■— for 1-Heptanol at 3.00 GHz.
System IV (a) —◑—◑— for 1-Decanol at 24.33 GHz.
IV (b) —⊙—⊙— for 1-Decanol at 9.25 GHz.
IV (c) —⊕—⊕— for 1-Decanol at 3.00 GHz.

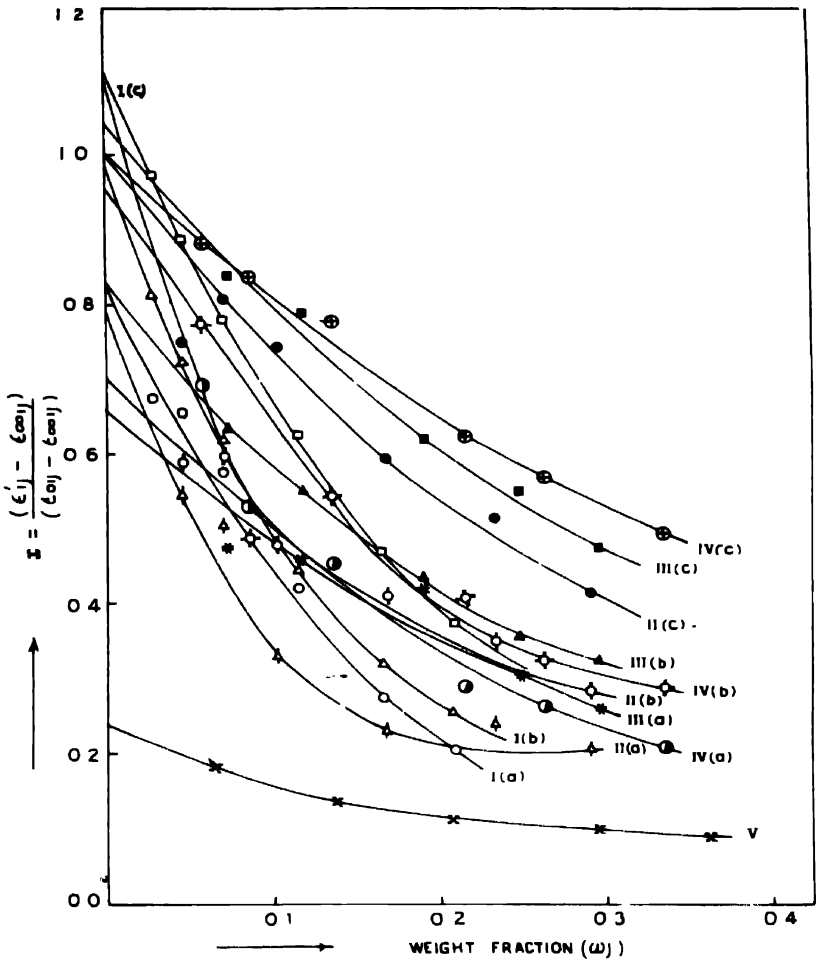

Figure 2. Variation of $(\varepsilon'_{ij} - \varepsilon_{\infty ij})/(\varepsilon_{0ij} - \varepsilon_{\infty ij})$ against weight fraction w_j for monoalcohols at different *uhf* electric field.

System I (a) —O—O— for 1-Butanol at 24.33 GHz
I (b) —Δ—Δ— for 1-Butanol at 9 25 GHz
I (c) —□—□— for 1-Butanol at 3 00 GHz
System II (a) for 1-Hexanol at 24 33 GHz
II (b) for 1-Hexanol at 9 25 GHz.
II (c) for 1-Hexanol at 3 00 GHz.
System III (a) for 1-Heptanol at 24 33 GHz
III (b) for 1-Heptanol at 9 25 GHz.
III (c) for 1-Heptanol at 3 00 GHz
System IV (a) for 1-Decanol at 24 33 GHz.
IV (b) for 1-Decanol at 9.25 GHz
IV (c) for 1-Decanol at 3 00 GHz.
System V —×—×— for 1-Ethanol at 9.84 GHz.

Putting $\frac{\varepsilon'_{ij} - \varepsilon_{\infty ij}}{\varepsilon_{0ij} - \varepsilon_{\infty ij}} = x$ and $\frac{\varepsilon''_{ij}}{\varepsilon_{0ij} - \varepsilon_{\infty ij}} = y$ with $\omega\tau = \alpha$ and using the abbreviations, $a = \frac{1}{1 + \alpha^2}$ and $b = \frac{\alpha}{1 + \alpha^2}$, the above eqs. (2) and (3) can be written as

$$x = c_1 a_1 + c_2 a_2, \tag{4}$$

$$y = c_1 b_1 + c_2 b_2, \tag{5}$$

where suffices 1 and 2 with a and b are related to τ_1 and τ_2 respectively. From eqs. (4) and (5), since $\alpha_2 - \alpha_1 \neq 0$ and $\alpha_2 > \alpha_1$ we have

$$c_1 = \frac{(x\alpha_2 - y)(1 + \alpha_1^2)}{\alpha_2 - \alpha_1} \tag{6}$$

$$c_2 = \frac{(y - x\alpha_1)(1 + \alpha_2^2)}{\alpha_2 - \alpha_1} \tag{7}$$

Now, using $c_1 + c_2 = 1$, one gets the following equation with the help of eqs. (6) and (7):

$$\frac{1 - x}{y} = (\alpha_1 + \alpha_2) - \frac{x}{y}\alpha_1\alpha_2$$

which, on substitution of the values of x, y and α yields

$$\frac{\varepsilon_{0ij} - \varepsilon'_{ij}}{\varepsilon'_{ij} - \varepsilon_{\infty ij}} = \omega(\tau_1 + \tau_2)\frac{\varepsilon''_{ij}}{\varepsilon'_{ij} - \varepsilon_{\infty ij}} - \omega^2\tau_1\tau_2. \tag{8}$$

Equation (8) is a straight line between $\frac{\varepsilon_{0ij} - \varepsilon'_{ij}}{\varepsilon'_{ij} - \varepsilon_{\infty ij}}$ and $\frac{\varepsilon''_{ij}}{\varepsilon'_{ij} - \varepsilon_{\infty ij}}$ with slope $\omega(\tau_1 + \tau_2)$ and intercept $-\omega^2\tau_1\tau_2$ respectively. Here, ω = angular frequency of the applied electric field of frequency f in GHz. When the eq. (8) is fitted with the measured dielectric relaxation data ε'_{ij}, ε''_{ij}, ε_{0ij} and $\varepsilon_{\infty ij}$ for different weight fractions w_j's of each alcohol in n-heptane (at 25°C under 24.33, 9.25 and 3.00 GHz electric fields) as well as of methanol and ethanol in benzene (at 9.84 GHz), we get the slopes and intercepts as shown in Table 1, to yield τ_1 and τ_2.

The relative contributions c_1 and c_2 towards the dielectric relaxations in terms of x, y and τ_1, τ_2 for each alcohol are found out and shown in Table 2. The theoretical values of x and y are, however, calculated from Fröhlich's equations [17] as

$$x = \frac{\varepsilon'_{ij} - \varepsilon_{\infty ij}}{\varepsilon_{0ij} - \varepsilon_{\infty ij}} = 1 - \frac{1}{2A}\ln\left(\frac{e^{2A}\omega^2\tau_s^2 + 1}{1 + \omega^2\tau_s^2}\right), \tag{9}$$

and

$$y = \frac{\varepsilon''_{ij}}{\varepsilon_{0ij} - \varepsilon_{\infty ij}} = \frac{1}{A}\left[\tan^{-1}(e^A\omega\tau_s) - \tan^{-1}(\omega\tau_s)\right], \tag{10}$$

Table 3. The estimated intercept (α) and slope (β) of $K_{ij} - w_j$ equation with correlation coefficient (r) and percentage of error, dimensionless parameters β's and dipole moments μ_j's with theoretical μ's and μ calculated by using the relation $\mu_1 = \mu_2(c_1/c_2)^{1/2}$ at 25°C of monoalcohols under different hf electric field

System with Sl. no. and Mol. wt. of solute	Frequency f in GHz	Intercept and slope of $K_{ij} - w_j$ eqn.		Correlation coeff (r)	% of error in regre tech.	Dimensionless parameters			Estimated dipole moments in Debye				
		$\alpha \times 10^{-10}$ in e.s u.	$\beta \times 10^{-10}$ in e.s u.			$b_0 = \frac{1}{1+\omega^2\tau_0^2}$	$b_2 = \frac{1}{1+\omega^2\tau_2^2}$	$b_1 = \frac{1}{1+\omega^2\tau_1^2}$	μ_0	μ_2	μ_1	μ_{theo}	$\mu_1 = \mu_2\left(\frac{c_1}{c_2}\right)^{1/2}$
I) 1-Butanol in	(a) 24.33	2.3523	1 2679	0 9978	0.12	0 2777	0 0142	0.9115	1.97	8.75	1.09		3.70
n-heptane	(b) 9 25	0.8941	0 5400	0 9997	0.01	0.4382	0 0278	0.9552	1 66	6.62	1.13	1 49	3.43
M_j = 74 gm	(c) 3.00	0.2887	0.2338	0 9999	0.00	0 5942	0.0593	0.9715	1.65	5.23	1.29		3.37
II) 1-Hexanol	(a) 24 33	2.3522	0.8192	0.9961	0.21	0.3279	0.0239	0.9066	1.72	6.36	1.03		3.06
in n-heptane	(b) 9 25	0.8929	0 4005	0 9997	0 01	0.4804	0.0392	0.9545	1.61	5.63	1.14	1.31	3.18
M_j = 102 gm	(c) 3.00	0.2889	0.1695	0.9999	0.00	0 6006	0.0633	0.9710	1.64	5.06	1.29		3.31
III) 1-Heptanol	(a) 24.33	2.3169	0 8276	0.9927	0 40	0 2611	0.0169	0.8788	2.06	8.10	1 12		3.54
in n-heptane	(b) 9.25	0.8973	0.3555	0 9993	0.04	0 5196	0.0412	0.9646	1.55	5 52	1 14	1.22	3 20
M_j = 116 gm	(c) 3.00	0.2891	0 1519	0.9997	0 01	0.5946	0 0607	0.9708	1.67	5.22	1 30		3.38
IV) 1-Decanol	(a) 24.33	2.3575	0.5787	1 0002	0 01	0 2870	0.0396	0.7973	1.92	5.17	1.15		2 76
in n-heptane	(b) 9.25	0.8949	0.2609	0.9966	0 18	0.3885	0 0411	0 9040	1.79	5.52	1.18	0 95	3 04
M_j = 158 gm	(c) 3 00	0 2894	0 1151	0 9997	0.01	0 7509	0 1327	0.9834	1.51	3.58	1 32		2 92
V) Ethanol in benzene													
M_j = 46 gm	9.84	1.1925	0 1977	0 9927	0.44	0 1831	0.00001	0 9997	1 19	147 19	0 51	1 67	14 50
VI) Methanol in benzene													
M_j = 32 gm	9.84	1 2058	0.2161	0 9928	0 43	—	0 00002	—	—	88.17	—	1 76	—

where A = Fröhlich parameter = $\ln(\tau_2/\tau_1)$ and τ_s is called the small limiting relaxation time being given by $\tau_s = \tau_1$. A simple graphical extrapolation technique, on the other hand, has been adopted here to get the values of x and y at $w_j \to 0$, as illustrated graphically in Figures 2 and 3 respectively. This is really in accord with Bergmann's eqs. (2) and (3) when the once estimated τ_1 and τ_2 from eq. (8) are substituted in the right hand sides of the above eqs. (2) and (3).

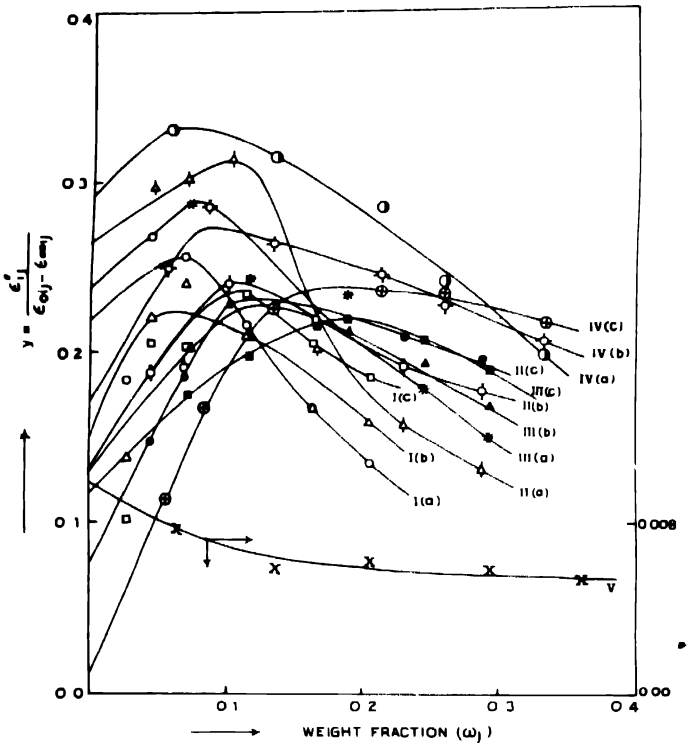

Figure 3. Variation of $\varepsilon''_{ij}/(\varepsilon_{0ij} - \varepsilon_{\infty ij})$ against weight fraction w_j for monoalcohols at different *uhf* electric field

System I (a) —O—O— for -Butanol at 24 33 GHz
I (b) —Δ—Δ— for -Butanol at 9 25 GHz
I (c) —□—□— for -Butanol at 3 00 GHz
System II (a) —◇—◇— for -Hexanol at 24 33 GHz
II (b) —○—○— for -Hexanol at 9 25 GHz
II (c) —●—●— for -Heptanol at 3 00 GHz
System III (a) —✱—✱— for -Heptanol at 24 33 GHz.
III (b) —▲—▲— for -Heptanol at 9 25 GHz.
III (c) —■—■— for -Heptanol at 3 00 GHz.
System IV (a) —◐—◐— for 1-Decanol at 24 33 GHz.
IV (b) —✲—✲— for 1-Decanol at 9 25 GHz.
IV (c) —⊕—⊕— for 1-Decanol at 3.00 GHz.
System V for 1-Ethanol at 9.84 GHz.

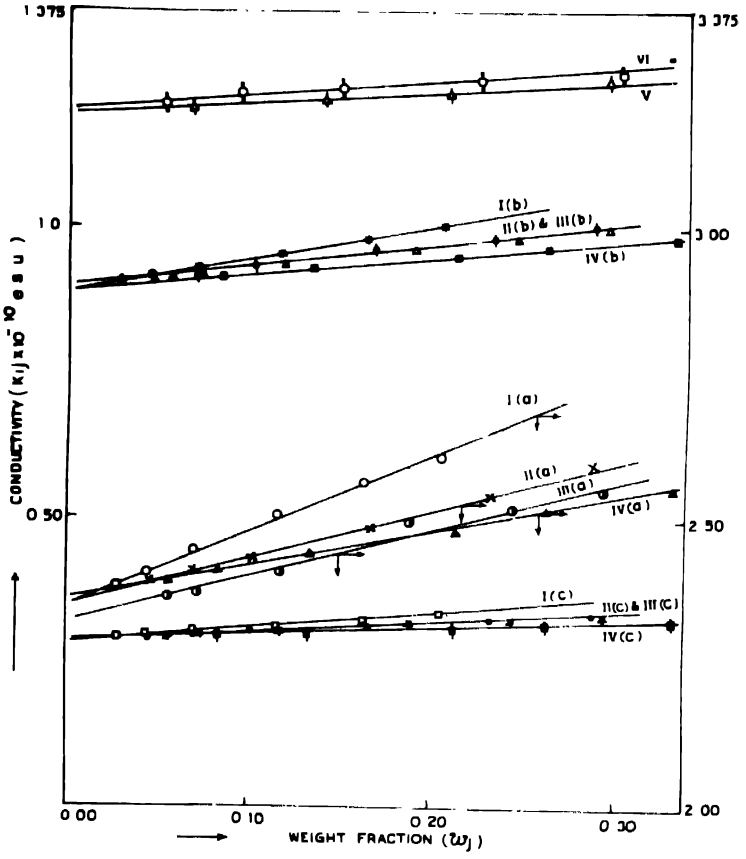

Figure 4. Straight line plots of K_{ij} against w_j under different *uhf* electric field at 25°C

System I (a)	—O—O—	for 1-Butanol at 24.33 GHz
I (b)	—✳—✳—	for 1-Butanol at 9.25 GHz
I (c)		for 1-Butanol at 3.00 GHz
System II (a)		for 1-Hexanol at 24.33 GHz
II (b)	—●—●	for 1-Hexanol at 9.25 GHz
II (c)		for 1-Heptanol at 3.00 GHz
System III (a)		for 1-Heptanol at 24.33 GHz
III (b)	-Δ- -Δ-	for 1-Heptanol at 9.25 GHz
III (c)	-✱- -✱-	for 1-Heptanol at 3.00 GHz
System IV (a)	-▲- -▲-	for 1-Decanol at 24.33 GHz
IV (b)		for 1-Decanol at 9.25 GHz
IV (c)	—■—■—	for 1-Decanol at 3.00 GHz
System V	—Δ—Δ—	for Ethanol at 9.84 GHz
System VI	—○—○—	for Methanol at 9.84 GHz

The dipole moments μ_1 and μ_2 of polar solutes in terms of τ_1 and τ_2 as obtained from the double relaxation method and slope β of the concentration variation of the experimental

uhf conductivity K_{ij} are then estimated. The uhf conductivity K_{ij} is, however, given by Murphy and Morgan [19] as

$$K_{ij} = \frac{\omega}{4\pi}\left(\varepsilon_{ij}''^2 + \varepsilon_{ij}'^2\right)^{1/2}, \tag{11}$$

which is a function of w_j of polar solute. Although $\varepsilon_{ij}'' < \varepsilon_{ij}'$ in the uhf electric field, still the term ε_{ij}'' offers resistance to polarisation. Thus, the real part K_{ij}' of the uhf conductivity of a polar-nonpolar liquid mixture at T°K can be written according to Smyth [20] as :

$$K_{ij}' = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3M_j kT}\left(\frac{\omega^2\tau}{1+\omega^2\tau^2}\right)w_j. \tag{12}$$

Differentiating the above eq. (12) with respect to w_j and for $w_j \to 0$, the eq. (12) reduces to

$$\left(\frac{dK_{ij}'}{dw_j}\right)_{w_j \to 0} = \frac{\mu_j^2 N \rho_i F_i}{3M_j kT}\left(\frac{\omega^2\tau}{1+\omega^2\tau^2}\right), \tag{13}$$

where, M_j is the molecular weight of a polar solute, N is the Avogadro's number, k is the Boltzman's constant, the local field $F_{ij} = \frac{1}{9}(\varepsilon_{ij}+2)^2$ becomes $F_i = \frac{1}{9}(\varepsilon_i+2)^2$ and the density $\rho_{ij} \to \rho_i$ the density of solvent at $w_j \to 0$.

Again, the total uhf conductivity $K_{ij} = \frac{\omega}{4\pi}\varepsilon_{ij}'$ can now be written as :

$$K_{ij} = K_{\infty ij} + \frac{1}{\omega\tau}K_{ij}'$$

or,
$$\left(\frac{dK_{ij}'}{dw_j}\right)_{w_j \to 0} = \omega\tau\left(\frac{dK_{ij}}{dw_j}\right)_{w_j \to 0} = \omega\tau\beta, \tag{14}$$

where β is the slope of $K_{ij} - w_j$ curve at infinite dilution, From eqs. (13) and (14) we thus get

$$\mu_j = \left(\frac{3M_j kT\beta}{N\rho_i F_i \omega b}\right)^{1/2} \tag{15}$$

in order to obtain the dipole moment in terms of b, where b is a dimensionless parameter given by

$$b = \frac{1}{1+\omega^2\tau^2}. \tag{16}$$

The computed μ_1, μ_2 and μ_0 together with b_1, b_2 and b_0 and β's of $K_{ij} - w_j$ equations for all the alcohols are given in Table 3.

3. Results and discussions

The least-square-fitted straight line equations of $(\varepsilon_{0ij} - \varepsilon'_{ij})/(\varepsilon'_{ij} - \varepsilon_{\infty ij})$ against $\varepsilon''_{ij}/(\varepsilon'_{ij} - \varepsilon_{\infty ij})$ for different weight fractions w_j's of 1-butanol, 1-hexanol, 1-heptanol and 1-decanol in n-heptane under alternating electric field of 24.33, 9.25 and 3.00 GHz at 25°C are shown in Figure 1, together with the experimental points on them. The straight line equations of methanol and ethanol in benzene at 9.84 GHz are :

$$\frac{\varepsilon_{0ij} - \varepsilon'_{ij}}{\varepsilon'_{ij} - \varepsilon_{\infty ij}} = 198.2809 \frac{\varepsilon''_{ij}}{\varepsilon'_{ij} - \varepsilon_{\infty ij}} + 5.4003$$

and

$$\frac{\varepsilon_{0ij} - \varepsilon'_{ij}}{\varepsilon'_{ij} - \varepsilon_{\infty ij}} = 288.7386 \frac{\varepsilon''_{ij}}{\varepsilon'_{ij} - \varepsilon_{\infty ij}} - 4.5211 \quad \text{respectively.}$$

The experimental data of $(\varepsilon_{0ij} - \varepsilon'_{ij})/(\varepsilon'_{ij} - \varepsilon_{0ij})$ for methanol and ethanol are so high that they can not be plotted in Figure 1. In absence of reliable values of ε_{0ij} and $\varepsilon_{\infty ij}$ for methanol, it is not possible to show the applicability of simple mixing rule in determining relaxation data for this system. But the method has been applied to ethanol and it is found that the τ value is 3207.57 p Sec which is in good agreement with the measured data as presented in Table 1. The weight fractions w_j's of the respective solutes have been obtained from mole fractions x_i and x_j of the solvent and solute of molecular weights M_i and M_j respectively by a relation [21]

$$w_j = \frac{x_j M_j}{x_i M_i + x_j M_j} \tag{17}$$

The linearity of all the straight lines, as illustrated in Figure 1; is, however, tested by evaluating their correlation coefficient r. They are found to lie within the range of 0.9638 to 0.6195 as shown in Table 1. The corresponding percentage of errors in the fitting technique, can be had from the correlation coefficients. They are all shown in the 5-th and the 6-th columns of Table 1 respectively. The errors, are, however, large in magnitudes in the hf electric field of 24.33 GHz for 1-hexanol, 1-heptanol and 1-decanol respectively, probably due to unavoidable uncertainty in measurements of relaxation parameters for such higher frequency.

τ_2 and τ_1 for each alcohol are estimated from the slope and the intercept of straight line eq. (8) and are placed in the 7-th and the 8-th columns of Table 1 respectively. All the monoalcohols show τ_2 and τ_1 at all the frequencies with an exception for methanol which exhibits the monorelaxation behaviour [12].

The monorelaxation behaviour [12] can easily be evaluated on the basis of the relaxation parameters by putting $c_1 = 0$ in eqs. (2) and (3). The resulting equation becomes :

$$\frac{\varepsilon_{0ij} - \varepsilon'_{ij}}{\varepsilon'_{ij} - \varepsilon_{\infty ij}} = \omega\tau_2 \frac{\varepsilon''_{ij}}{\varepsilon'_{ij} - \varepsilon_{\infty ij}}. \tag{18}$$

τ_2 for methanol is found to be 5254.3 p Sec in approximate agreement with τ_2 as obtained by double relaxation method (Table 1). τ_2's and τ_1's as obtained from the double relaxation method are then compared with the most probable relaxation time τ_0 where $\tau_0 = \sqrt{\tau_1 \tau_2}$ and the measured relaxation time τ_s's from the slope of the given relation :

$$K''_{ij} = K_{\infty ij} + \frac{1}{\omega \tau_s} K'_{ij}, \tag{19}$$

where $K_{\infty ij}$ is the constant conductivity at infinite dilution. Both τ_0 and τ_s are shown in the 10-th and the 9-th columns of Table 1, respectively. τ_2 and τ_1 for the double relaxation processes show low values at 24.33 GHz and increase gradually at the lower frequencies of

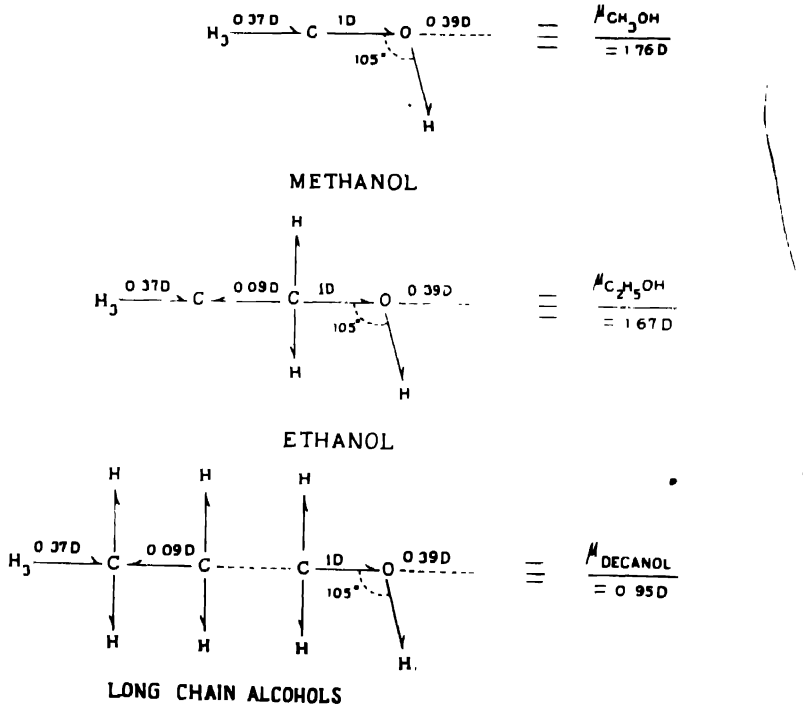

Figure 5. Conformational structures of methanol, ethanol and decanol

9.25 and 3.00 GHz respectively. This is explained on the basis of the fact that at higher frequency, the rate of hydrogen bond rupture in long chain alcohols may be maximum to reduce τ for each rotating unit. This sort of behaviour is also observed in the estimated τ_s and τ_0 respectively. Although, the measured τ_s and τ_0 are smaller in magnitudes, τ_1 agrees excellently with τ_s (Table 1). This is perhaps due to the fact that the hf conductivity measurement always yields the average microscopic relaxation time whereas the double relaxation phenomena offers a better understanding of microscopic as well as macroscopic molecular relaxation times.

The relative contributions c_1 and c_2 towards dielectric relaxations for each alcohol have been evaluated from Bergmann's eqs. (2) and (3) for fixed values of τ_1 and τ_2 as predicted by eq. (8), with the estimated x and y from graphical technique as well as from Fröhlich's eqs. (9) and (10) respectively. c_1 and c_2 thus obtained by Fröhlich's method are placed in the 6-th and 7-th columns of Table 2. In the 10-th and the 11-th columns of the same Table 2 are shown c_1 and c_2 values with the fixed values of x and y at infinite dilutions of Figures 2 and 3. The variations of x and y with w_j are concave and convex in nature as illustrated graphically in Figures 2 and 3 in accordance with Bergmann's eqs. (2) and (3) respectively. Ethanol is an exception whose y value changes in a similar way as x. This anomaly is perhaps due to nonavailability of the accurate ε_{0ij} and $\varepsilon_{\infty ij}$ [11], and it thereby yields abnormally high τ value like methanol, although the latter one exhibits monorelaxation behaviours as shown in Table 1. However, the estimated value of c_2 is greater than c_1 for each alcohol, under investigation, in Fröhlich's method, while the reverse is true for the graphical method. Eventually, c_2 is -ve for most of the cases except 1-hexanol at 24.33 GHz and ethanol at 9.84 GHz respectively in the latter case. This –ve value of c_2 is due to inertia of the flexible part [10]. This type of behaviour may be explained on the basis of the fact that the latter one ascertains the nature of the flexible part in comparison to Fröhlich's method. It is also interesting to note that unlike Fröhlich's method, the latter method yields $c_1 + c_2 < 1$ except for 1-decanol at 24.33 GHz where $c_1 + c_2 < 0$, although $|c_1 + c_2| > 1$ signifying more than two relaxation processes may be possible in them [14].

The dipole moments μ_1 and μ_2 of all the alcohols, as enlisted in Table 3, were estimated in terms of dimensionless parameters b_1 and b_2 and slopes β of K_{ij} *versus* w_j equations by using eq. (15). The linear variation of uhf conductivities K_{ij} of all the alcohols as a function of w_j's are shown in Figure 4. The correlation coefficient r and the corresponding percentage of error in the estimation of the slope β and hence all the μ's together with b's are shown in Table 3. From Table 3, μ_2's are, however, found to be large at 24.33 GHz while in comparatively lower frequencies like 9.25 and 3.00 GHz, they are gradually smaller for each polar alcohol under our investigation. But μ_1's, on the other hand, show the opposite trend. It is also interesting to note that the values of μ_2's for all the alcohols decrease with the increase of C-atoms in them. This type of behaviour may be explained by the fact that the long chain polymer type molecules having a large number of carbon atoms, in a nonpolar solvent, tend to break up in the hf electric field in order to reduce or even eliminate the absorption attributable to them. The proportion of smaller molecular species, on the other hand, have comparatively smaller number of C-atoms and the corresponding absorption will increase [14]. This is also confirmed by the fact that as τ decreases with increasing ω, the term $\omega^2\tau^2$ is higher and therefore, eq. (16) yields smaller b values to increase μ's according to eq. (15).

μ_1, μ_2 and μ_0 are finally compared with μ_{theo} for the orientational polarisation of all the associated liquids containing a large number of dipolar groups like $H_3 \rightarrow C$, $C \leftarrow O$ and $O \leftarrow H$ when their individual monomeric moments are added vectorially as shown in Figure 5. μ_{theo} may also be inferred from Fröhlich's equation having correlation factor which bears structural information for such liquids. But to a fair approximation, the structural conformation of such liquids, as shown diagrammatically in Figure 5 and placed in Table 3, from the bond moments of $H_3 \rightarrow C$, $C \leftarrow O$ and $O \leftarrow H$ and the bond angle of 105° made by –OH groups with the main bond axis, have the major contributions in yielding the theoretical dipole moment, μ_{theo}. All the μ's are displayed in Table 3 with those of μ_1, where $\mu_1 = \mu_2\left(\frac{c_1}{c_2}\right)^{1/2}$, assuming the two relaxation processes are equally probable. These μ_1's are slightly larger in magnitudes in comparison to μ_{theo}, μ_1 and μ_0 which are in close agreement among themselves.

4. Conclusion

The methodology so far advanced for double and single broad dispersions of the polar-nonpolar liquid mixtures seems to be much simpler, straightforward and significant one to detect the existence of double and monorelaxation behaviours of polar liquids in nonpolar solvents. The correlation coefficients between the desired parameters as given in eqs. (8) and (18) could, however, be estimated to find out the percentage of errors entered in the dielectric relaxation data, to yield τ_1 and τ_2 of the polar liquids, because the relaxation times τ's are claimed to be accurate within ± 10%. The monohydric alcohols so far studied always yield, both τ_1 and τ_2 at all frequencies of the electric field. The corresponding dipole moments μ_1 and μ_2 can then be estimated from eq. (15) in terms of b_1 and b_2 (which are, however, related to τ_1 and τ_2 as estimated) to arrive at their conformations as shown in Figure 5.

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Appendix

List of nomenclature used :

ε_{ij}, ε_{ij}	real and imaginary parts of the complex dielectric constant ε^*_{ij} of a solution,
$\varepsilon^*_{ij} = \varepsilon'_{ij} - j\varepsilon''_{ij}$	where $j = \sqrt{-1}$ is a complex number,
ε_{0ij}, $\varepsilon_{\infty ij}$	static and optical dielectric constants of the solution,
$\omega = 2\pi f$	angular frequency of the applied electric field, f being the frequency in Hertz,
K'_{ij}, K''_{ij}	real and imaginary parts of the complex electrical conductivity K^*_{ij} of a solution,
$K^*_{ij} = K'_{ij} + jK''_{ij}$	where $j = \sqrt{-1}$ is a complex number,
$K_{\infty ij}$	constant conductivity of the solution at $w_j \to 0$,
μ_j	dipole moment of the j-th type of solute,
μ_1, μ_2	dipole moments of the flexible part and the whole molecule,
τ_s	relaxation time of the solute,
τ_1, τ_2	relaxation times of the flexible part and the whole molecule,

τ_0	most probable relaxation time of the solute,
$A = \ln(\tau_2/\tau_1)$	the Fröhlich parameter,
w_j	weight fraction of the solute,
c_1, c_2	relative contributions due to τ_1 and τ_2 respectively,
M_j	molecular weight of the j-th type of solute,
β	slope of the $K_{ij} - w_j$ curve.